LASER-INDUCED FLUORESCENCE AND TIME-RESOLVED EMISSION SPECTROSCOPY OF LASER ABLATION PLASMA

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Pulsed laser ablation plasmas produced by high power laser radiation near a solid target have numerous applications [1]. These include deposition of thin layers, vaporization of sample material for spectrochemical analysis, formation of atomic molecular and cluster beams etc. For optimization of these applications it is of great importance the understanding the basic physical and chemical processes governing the plasma composition at the various stages of its evolution.

The distinctive feature of pulsed laser ablation plasma is a complex spatio-temporal structure and a wide range of varying of plasma parameters during the plasma existence time. The plasma parameters are heavily dependent on irradiation conditions such as incident laser fluence, irradiation spot dimension, environment atmosphere composition and pressure. In a study of such plasmas one has to cope with a combination of short time scales (ns), small spatial dimensions (mm) and consequently strong plasma density gradients and the low density of the active species. In order to obtain the quantitative information on plasma parameters, like electron temperature, electron density, spatial and temporal evolution of transient species the currently available techniques should be adopted and laser aided diagnostics must be developed, which combine high sensitivity with a good spatial and temporal resolution.

In the present paper the laser-induced fluorescence method (LIF) combined with the time resolved emission spectroscopy was adopted to measure the spatial and temporal distributions of ions, atoms, and molecules, electron temperature and density in the laser ablation plasma. The developed spectroscopic diagnostics allowed to overcome the existing sensitivity limitations**,** to improve the time and space resolution, and to simplificate of modeling assumptions.

Plasma was produced by focusing of a Nd:YAG laser radiation (1064nm, 10ns, 10^8-10^9 W/cm^2) on the surface of the metallic (Al, Ti) and graphite samples in the helium (air) atmosphere at pressures of 10^{-3}-500 Torr. The details about the densities, temperatures, time-

space distributions of various ablated species (Al, Al^+, Ti, Ti^+, AlO, TiO, C_2) were obtained. The quantitative interpretation of LIF measurements was performed by using the three-level atomic and four-level molecular approximations, the measured collisional quenching rates of the excited states as well as taking into account the shape of the excitation laser pulse and the temporal variation of the absorption linewidth.

The electron density (n_e) was determined from the emission linewidth measurements according to the Stark broadening theory. The shapes of some selected lines were analyzed at different delay times (with respect to the leading edge of the laser pulse) in order to obtain the temporal evolution of n_e. The electron temperature (T_e) was deduced by the relative intensities of lines from a given state of ionization.

Optical observation of the plasma emission was performed by imaging the section of the plasma plume onto the entrance slit of monochromator equipped by the fast photomultiplier. The emission spectra of plasma were recorded in the UV and visible region (spectral resolution of $\Delta\lambda \geq 3\times10^{-2}$nm) at different distances from the target surface. The detection of the photomultiplier signals was accomplished by a transient digitizer, connected to a personal computer for data processing, storage and analysis.

For LIF measurements a tunable dye laser radiation at the fundamental wavelength (560 - 630 nm) or its second harmonic was used to probe the ground state atoms and ions with the regular delay times after ablating laser pulse.

The emission spectra, electron temperature and density were found to be influenced by the irradiation conditions and ambient atmosphere. For example, the temporal evolution of electron density deduced from Stark broadening of the AlI 396.15nm line in the aluminum/air plasma and time dependence of electron temperature are shown in the Fig.1. The measured values of n_e are in the range of 1.4×10^{18} -3.5×10^{17} cm^{-3} in the time interval of 0.3 - 0.6μs after the laser pulse, while the electron temperature drops from 1.6 eV to 1 eV. The electron temperature rapidly decreases in the time interval where maximal line emission is observed. After this time T_e begins to decrease more slowly, showing that there is a quasistationary equilibrium between the rates of cooling of electrons and their recombination heating.

The absolute measurements of concentrations of atoms, ions and molecules in laser ablation plasmas were performed by the LIF method. The temporal profiles of atoms and ions in the plume were in the form of curves (Fig. 2) with maxima whose value and position were dependent on the conditions of focusing of radiation onto the target. The observed temporal

profiles are formed predominantly by recombination processes and cannot be explained by only the time-of-flight characteristics of the plasma. The range of the concentrations of Ti atoms of 2×10^{13}-1.1×10^{15} cm^{-3} and ions of 2.5×10^{12}-4.5×10^{13} cm^{-3} was recorded in the titanium/air plasma. TiO molecules were detected at the stages of plasma expansion and afterglow in the time interval of 5-60 μs after ablation laser pulse and up to 3 mm from the target surface (Fig.2). With the plasma evolution the density decreases up to 1 10^{13} cm^{-3} (60 μs) as well as with increasing of a distance from a target.

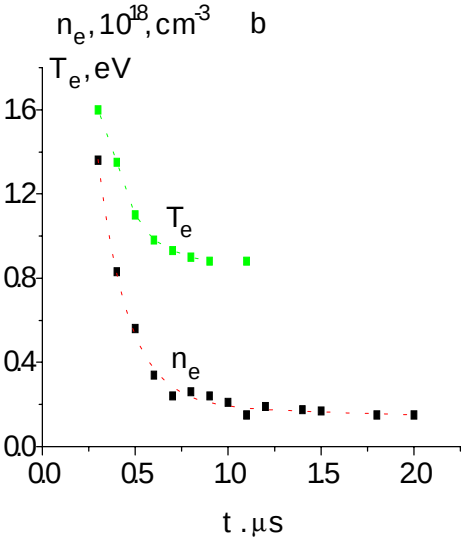

Fig. 1. Time evolution of electron density (n_e) and temperature (T_e) in aluminum/air plasma at distance of 0.5mm from the target and laser irradiance of 500 MW/cm^2.

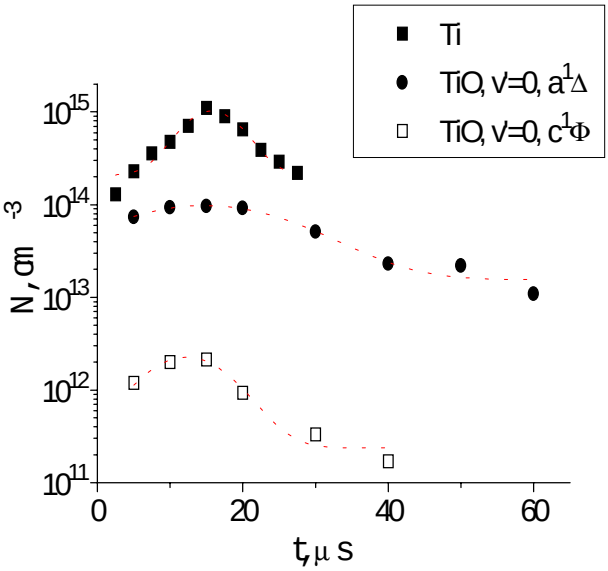

Fig. 2. Concentrations of the ground state Ti atoms and TiO molecules in states $a^1\Delta$, v'=0 (•) and $c^1\Phi$, v''=0 (❑) in the titanium/air plasma as a function of the delay from the ablation laser pulse.

Based on the results of quantitative diagnostics fundamental processes (recombination, chemical reactions, cluster formation) which determine the plasma composition evolution were analyzed and the correlation of these processes with initial conditions of plasma creation were established.

The temporal evolution of densities of electrons and excited atoms are discussed in terms of three-body electron-ion recombination, ionization and gasdynamical expansion. Dynamics of recombination indicated a very slow recombination of ions with electrons in the late stage of plasma decay. The characteristic recombination time essentially exceeded the gasdynamical expansion one. So, plasma has had time to fly apart without a complete recombination (situation of "frozen" ionization). The conservation of charged particles in the

late stages may be favorable to the intensification of clustering process because the ions become the centers of condensation.

The formation of C_2 and C_3 molecules in laser ablation carbon plasma was investigated by LIF monitoring of the time-space distributions of these molecules in the plasma. The presence of C_2 and C_3 molecules in plasma was considered to be as a first step in the formation of carbon clusters. The emission spectrum is dominated by the C_2 Swan bands ($d^3\Pi_g$ - $a^3\Pi_u$) in the Δv = -2; -1; 0; +1; +2 sequences. The emission spectra in the wavelength range 390 - 410 nm can be identified as the C_3 bands. The C_2 high pressure bands in the spectra were recorded including the (6 - 7) band at 543.4 nm and (6 - 8) band at 589.9 nm. These bands were thought to be either thermally excited or formed from atomic carbon recombination. Estimates of vibrational temperatures of C_2 species under various helium pressures support that, the recombination of free carbon atoms is the most likely mechanism for the production of C_2 molecules.

So, the experiments performed demonstrate the great diagnostic capabilities of the LIF combined with the time resolved emission spectroscopy for the analysis of plasma dynamics during the laser-induced ablation of solid samples. Based on the quantitative data provided by LIF measurements the details about the densities, temperatures and kinetic energies of various ablated species were obtained. The experimental results show a rather complex evolution of plume particles. In the initial stage of plasma decay the gas dynamical expansion and recombination processes play a major role in plasma evolution. The possibility of plasma decay regime with a frozen ionization state in the late stages has been shown. The results permitted to elucidate the effects of oxidation kinetics and dimer (cluster) formations on the relative concentrations in ablation plasmas. The role of excited and metastable reagents in oxidation kinetics has also been established.

Acknowledgements

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Reference

[1] R.M. Gilgenbach, C.H. Ching, J.S. Lash, and R.A. Lindley: Phys. Plasmas **1** (1994) 1619.